

Double ChemFET for the In-Line Monitoring of Silver Dosing in Potable Water Systems

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With NASA Advanced Exploration Systems (AES) Life Support Systems (LSS) baselining ionic silver (Ag^+) as the biocide of choice, development in silver monitoring technologies becomes necessary to monitor and control Ag^+ release. Ion-selective field effect transistors (ISFETs) and chemically-sensitive field effect transistors (ChemFETs) are capable of selective detection of Ag^+ with reversible and low detection limit responses. However, one major hurdle to ChemFET technologies is the requirement of a reference electrode, which can leak its fill solution into the potable water system and is prone to drift requiring frequent calibration. To circumvent this issue, a double chemically-sensitive field effect transistor (dChemFET) is proposed. The dChemFET uses a second ChemFET to selectively monitor the counter ion and serves in place of the reference electrode. This work reports on the development of the dChemFET, starting with the development of the Ag^+ and NO_3^- ion selective membranes (ISMs) to be used in the ChemFETs. The Ag^+ ISM was tested in 50-10⁵ ppb Ag^+ and showed linear, sub-Nernstian response. The NO_3^- ISM was tested in 50-500 ppb silver ion equivalents of nitrate ion (Ag^+ equiv. of NO_3^-) and shows linear, sub-Nernstian response as well. However, the Ag^+ and NO_3^- ISMs face significant challenges in terms of drift that obstruct its application for long-term monitoring, but it can serve as a starting point for demonstrating the dChemFET proof of concept.

Nomenclature

Ag^+	=	silver ion	ISE	=	ion-selective electrode
AgCl	=	silver chloride	ISFET	=	ion-selective field effect transistor
AgNO_3	=	silver nitrate	ISM	=	ion-selective membrane
Ag_2S	=	silver sulfide	MBT	=	2-Benzothiazolethiol
ChemFET	=	chemically-sensitive field effect transistor	mL	=	milliliter
dChemFET	=	double chemically-sensitive field effect transistor	mV	=	millivolt
DBP	=	dibutyl phthalate	NaTPB	=	sodium tetraphenylborate
DOP	=	dioctyl phthalate	NO_3^-	=	nitrate ion
DTBBT	=	2,2'-dithiobis(benzothiazole)	OCP	=	open circuit potential
FET	=	field effect transistor	ppb	=	parts per billion
			Ag^+ equiv. of NO_3^-	=	silver ion equivalents of nitrate ion

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TetDDAN = tetradodecylammonium nitrate
TriDDMAN = tridodecylmethylammonium nitrate

TOAB = tetraoctylammonium bromide
THF = tetrahydrofuran

I. Introduction

ONGOING efforts to implement silver ions (Ag^+) as the biocide for the disinfection of potable water life support systems has created a desire for ionic silver monitoring. As ionic silver dosing technologies continue to be developed, NASA needs to control and monitor the Ag^+ concentration. A NASA trade study has identified three potential Ag^+ monitoring technologies (ion-selective electrodes (ISE), anodic stripping voltammetry, and fiber optic chemical sensors).¹ All three technologies were assessed to have significant obstacles to space implementation and as a result, no one technology was recommended for near-term implementation. In the case of ISEs, they provide excellent low ppb Ag^+ detection, small size, and simple design. However, ISEs require frequent calibration due to drift and require a reference electrode that poses risks in terms of leaking internal reference solution and consumable use.¹

ISEs function through a solid or liquid matrix referred to as an ion-selective membrane (ISM) that contains an ionophore (ion carrier) or ion exchanger to reversibly bind or interact with a primary ion (Ag^+ and NO_3^- in this application). The binding or interaction of the primary ion within the ISM induces a change in potential measured under zero current conditions (open circuit potential (OCP) measurements), which is referred to as the electromotive force (emf).² The factors controlling emf are found in eq. 1

$$emf = E_{const} + E_J + E_M \quad (1)$$

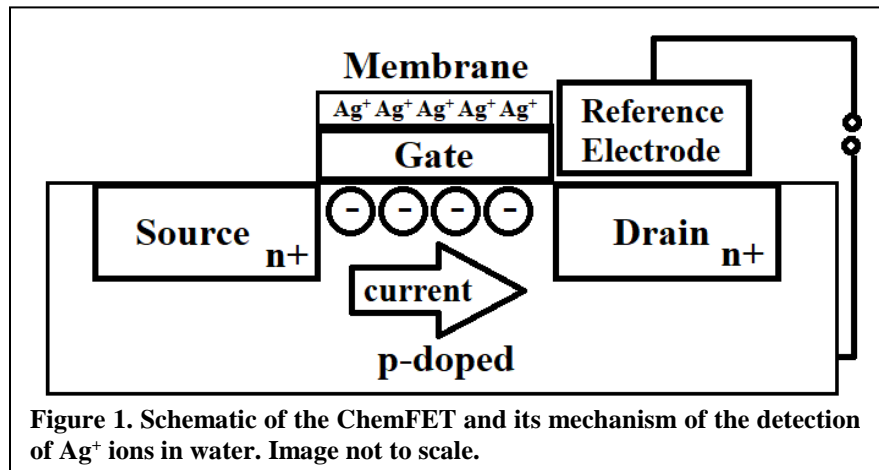
Where E_{const} is the potential contributions independent of the sample, E_J is the liquid junction potential of the sample/bridge electrolyte, and E_M is the membrane potential. E_J can be considered low in our use case as our conditions are low conductivity, deionized (DI) water and the only bridge electrolyte introduction is what leaks from the electrolyte solution within the reference electrode, which should be low with the exposure time of minutes for each measurement. As a result, E_M is considered the primary potential contribution to changes in the emf in ideal conditions and is the contributor of focus in emf or open circuit potential measurements. E_M can be expressed as a linear relationship to the log of the concentration of primary ions through the Nernst equation in eq. 2

$$E_M = E^0 + \frac{RT}{zF} \ln(a_A) = E^0 + 59.2 \log(a_A) \quad (2)$$

Where E^0 is the potential contributions independent of the sample, R is the universal gas constant (8.314 J/K*mol), T is temperature in Kelvin, z is the charge of the primary ion, F is the Faraday constant (96485 C/mol), and a_A is the activity of the primary ion. In the case of dilute conditions, activity can be related to the concentration of the primary ion. The slope in this equation ($2.303*RT/zF$) can be calculated and, in the case of room temperature, is expected to be 59.2 mV/decade (order of magnitude of concentration) for +1 primary ions like Ag^+ and to be -59.2 mV/decade for -1 primary ions like nitrate (NO_3^-). This potential is measured in the presence of a reference electrode, which is a significant obstacle to space implementation as stated in the silver monitoring trade study.¹

The NASA trade study also noted the reference electrode obstacle for ion-selective field effect transistors (ISFETs) and were not considered for further assessment in the trade study, as a result.¹ ISFETs are a field effect transistor (FET)-based technology for detecting ions. After the discovery of ISFETs, the concept of chemically-sensitive field

effect transistor (ChemFET) was used to extend this FET-based detection to all chemicals, including ions. Figure 1 shows the components of a ChemFET. This ChemFET contains n-type current source and drain, controlled by a constant voltage applied to these regions through electrical contacts (not depicted). The source and drain are separated by a p-doped silicon body with a gate insulator over the surface. In the case of ChemFETs, the gate is chemically modified or coated



with an ISM to bind with the primary ion. Positive ion accumulation within the ISM increases the potential of the membrane, which can be related to the Nernst equation (eq. 2). An increase in the potential over the gate insulator results in an electric field causing an increased accumulation of electron charges within the silicon body that create an n-channel, referred to as the enhanced region. This enhanced region allows for current flow from the source to the drain when the gate-source voltage exceeds the threshold voltage of the ChemFET. With higher potentials at the gate, the resulting electric field draws more electrons to the enhanced region, which creates a larger n-channel and increases the current. The ChemFET can apply two different types of detection methods for measuring changes in the enhanced region as a result of ion accumulation, either fixed applied voltage or constant drain current methods. For the fixed voltage method, the source-drain and source-reference electrode voltages are kept constant and the current of the ChemFET is measured. As a result of this fixed voltage, increases in the ion concentration reduces the resistance and increases the current of the enhanced region. For the constant drain current method, the drain current is kept constant through the use of an operational amplifier and changes in the output voltage correlate with changes in the primary ion concentration. As a result, ChemFETs apply ISE detection principles by monitoring of the changes in potential caused by ion accumulation in the ISM to induce changes in the enhanced region with the FET, resulting in changes in the measured current or voltage of the device. The reference electrode sets the gate voltage, typically with the reference electrode at 0 V (referred to as a grounded reference electrode).

One possible configuration for ChemFETs is the double ChemFET (dChemFET)³, which uses a second ChemFET that detects a background ion in place of a reference electrode. The difference in potentials of the primary ion ChemFET and the background ion ChemFET provides a potential measurement while removing the need for the reference electrode as seen in eq. 3.

$$\Delta E = (E_{Ag} - E_{ref}) - (E_{NO_3} - E_{ref}) = E_{Ag} - E_{NO_3} \quad (3)$$

Where ΔE is the potential difference between the Ag^+ and NO_3^- ChemFETs, E_{Ag} is the potential of the Ag^+ ChemFET, E_{NO_3} is the potential of the NO_3^- ChemFET, and E_{ref} is the reference electrode potential. Successful implementation of this concept for silver monitoring can circumvent the challenges and issues of using a reference electrode and makes this technology more viable for space applications.

In this early work, the development and testing of Ag^+ and NO_3^- ISMs to assess their use on ChemFET devices in a dChemFET configuration is reported. The chemicals used to make the ISMs are shown in Table 1. Ag^+ ISMs are prepared using four different Ag^+ ionophores shown in Table 1. ISMs with synthesized SI-2 are capable of detecting Ag^+ over the 50-10⁶ parts per billion (ppb) range with sub-Nernstian response (slope <58.2 mV/decade). DTBBT ISMs showed some initial success when tested over the 100-10⁶ ppb range with Nernstian responses, but was not repeatable on later runs. MBT and Porphine showed no success in linearly detecting Ag^+ . As a result, Silver Ionophore II was chosen out of the four Ag^+ ionophores tested to be used in the dChemFET proof of concept. For NO_3^- detection, ISMs were prepared using five different NO_3^- ionophores shown in Table 1. TetOAB, NI-6, and TetOAN were tested over 100-10⁵ ppb silver ion equivalents of nitrate ion (ppb Ag^+ equiv. of NO_3^-) due to the high limit of detection of these ionophores while TetDDAN and TriDDMAN were tested in 50-500 ppb Ag^+ equiv. of NO_3^- . The best-performing NO_3^- ISM was made with TetDDAN and shows a linear range when tested in 50-500 ppb Ag^+ equiv. of NO_3^- . As a result, ISMs made with Silver Ionophore II and

Table 1. ISM Chemicals and Abbreviations.

ISM Chemical	Abbreviation
Silver Ionophores	
Silver Ionophore II ^a	SI-2
2,2'-dithiobis(benzothiazole)	DTBBT
2-Benzothiazolethiol	MBT
5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine	Porphine
Nitrate Ionophores	
tetraoctylammonium bromide	TetOAB
Nitrate Ionophore VI	NI-6
tetraoctylammonium nitrate	TetOAN
tetradodecylammonium nitrate	TetDDAN
tridodecylmethylammonium nitrate	TriDDMAN
Polymer	
polyvinyl chloride	PVC
Plasticizers	
dibutyl phthalate	DBP
dioctyl phthalate	DOP
2-nitrophenyl octyl ether	NPOE
Additive	
sodium tetraphenylborate	NaTPB
Solvent	
tetrahydrofuran	THF

^a Ionophore synthesized in lab.

TetDDAN were considered the prime candidates for coating the gates of the primary and reference ChemFETs, respectively, in the dChemFET system. However, issues of drift continue to affect the performance of the TetDDAN ISM as the potentials measured continue to trend downward with each day of measurement. As a result, further studies into causes of ISM drift were made and experiments are in process for reducing this drift.

II. Methods and Materials

A. Silver Ionophore II Synthesis

The ionophore synthesis to produce Silver Ionophore II (SI-2; 6-Oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11-13-triene) is adapted from a high-dilution reaction in literature by Casabo.⁹ Reaction Solution A was made with potassium nitrate (0.01 mol; 0.5611 g) and 2-mercaptoethyl ether (0.005 mol; 0.6913 g) in 12.5 mL of ethanol. Reaction Solution B was made with α,α' -Dichloro-m-xylene (0.0067 mol; 1.1671 g) in 16.7 mL of ethanol. Each reaction solution was added dropwise simultaneously at an approximately 1 drop per minute rate into a stirring reaction vessel containing 250 mL of ethanol. Upon adding 8.3 mL of each reaction solution, the addition process was completed and the reaction was left overnight stirring. The reaction vessel solution was filtered to remove the precipitated potassium chloride and then evaporated to dryness. The oily product residue was dissolved with 25 mL hexane. The hexane was washed with sodium carbonate and water several times with the water fraction removed. Sodium sulfate was added to dry the hexane fraction and left overnight. The solution was then evaporated to dryness and the remaining ionophore product was stored.

B. Silver Nitrate Solution Preparation

10^6 ppb Ag^+ stock solution was prepared from silver nitrate (AgNO_3) by dissolving 0.1575 g AgNO_3 in 100 mL of deionized (DI) water. The stock solution was then diluted to the concentrations of interest. Testing for determining the linear detection range of all the Ag^+ ISMs was done using $100\text{-}10^6$ ppb Ag^+ solutions. After determining which ionophores were successful in detecting Ag^+ with a linear range including $100\text{-}10^3$ ppb, solutions of 50, 100, 200, 300, 400, and 500 ppb were made to test ISM performance at the expected space application range (200-400 ppb). For NO_3^- ISMs, testing was done with $50\text{-}10^5$ ppb Ag^+ equiv. of NO_3^- solutions.

The Ag^+ solution concentrations were confirmed in a calibration curve at the beginning of each testing day by measuring the solutions for open circuit potential (OCP) using a silver/silver sulfide (Ag/AgS) half-cell electrode (Orion 9416BN) as the working electrode and the silver (Ag)/silver chloride (AgCl) double junction electrode (Orion #90-02-00) as the reference electrode. The reference electrode inner filling solutions was Orion 900002 inner filling solution (potassium nitrate, potassium chloride, and sodium chloride) and the outer filling solution was either Orion 900003 outer filling solution (potassium nitrate) for Ag^+ testing or 0.1 M sodium sulfate for NO_3^- testing. If the measured potentials remains within $\pm 2\%$ the previous day's measurements on the same Ag^+ solutions and yields a fitted linear calibration curve that adheres to Nernstian behavior with a slope within 54-62 mV/decade, the solutions are considered ready for ISM testing.

C. Ion-Selective Membrane (ISM) and Ion-Selective Electrode (ISE) Preparation

SI-2 was synthesized following section II.A. Chemicals in Table 1 were purchased from Sigma-Aldrich. ISM solutions were prepared following Table 2 according to membrane compositions described in literature.^{4,9-13} Film mass % in the last column of Table 2 is defined by the percentage of sum of the masses of the ionophore, polymer, plasticizer, and additive ($m_{\text{ionophore}}$, m_{polymer} , $m_{\text{plasticizer}}$, m_{additive} , respectively) divided by the sum of these masses with the mass of the THF (m_{THF}) as shown in eq. 4

$$\text{Film mass \%} = \frac{(m_{\text{ionophore}} + m_{\text{polymer}} + m_{\text{plasticizer}} + m_{\text{additive}})}{(m_{\text{ionophore}} + m_{\text{polymer}} + m_{\text{plasticizer}} + m_{\text{additive}} + m_{\text{THF}})} * 100 \quad (4)$$

It should be noted that the literature on the SI-2 ISM solution had originally used a ~60:30 ratio of PVC:plasticizer⁹, but the formulation was adapted to use the ~30:60 PVC:plasticizer ratio commonly used in literature for the other Ag^+ ISMs. Each component was weighed into a 10 mL screw cap vial on an analytical balance and recorded. The order of addition of each component is the additive (if used), ionophore, PVC, plasticizer, PVC, and then THF. After the THF is added to the vial, the vial is immediately capped and then vortex mixed for at least 1 minute or until no granules of the PVC, ionophore, or additive are visible. One exception to this is Porphine, which showed poor solubility in the ISM solution with visible ionophore particles and the ISM was deposited while the ionophore dispersed in solution after vortex mixing.

ISMs were prepared by drop-casting ISM solution onto clean platinum (Pt) disc electrodes. When reusing a Pt disc electrode, the electrodes were cleaned of the previous ISM deposition using a THF wash, followed by polishing using 0.05 μm alumina in water suspension and a polishing pad. After polishing, the electrodes was sonicated in DI water and then washed alternating between isopropanol and ethanol.

Table 2. ISM Solution Preparation.

Ionophore Used	Ionophore mg (%)	PVC mg (%)	Plasticizer mg (%)	Additive mg (%)	THF mg	Film mass %
Ag ⁺ ISMs						
SI-2 ⁹	7.7 (7.0%)	35.8 (32.6%)	66.4 ^a (60.4%)	-	2745.3	3.8%
DTBBT ¹⁰	4.3 (2.0%)	67.9 (31.4%)	139.3 ^a (64.4%)	4.9 ^d (2.2%)	1776.3	10.4%
MBT ¹¹	4.1 (2.0%)	65.6 (31.8%)	132.2 ^a (64.2%)	4 ^d (2.0%)	6223	3.1%
Porphine ¹²	7.7 (3.5%)	64.4 (29.5%)	144.2 ^a (66.0%)	2.2 ^d (1.0%)	4445	4.5%
NO ₃ ⁻ ISMs						
TetOAB ¹³	10.1 (3.0%)	106.6 (31.7%)	220 ^b (65.3%)	-	2225	13.1%
NI-6 ⁴	10.8 (5.2%)	97.5 (47.3%)	96.5 ^b (46.8%)	1.4 ^e (0.7%)	5088.2	3.9%
TetOAN ²²	5.1 (2.9%)	49.8 (28.5%)	117.2 ^b (67.0%)	2.7 ^e (1.5%)	4916.8	3.4%
TetDDAN ¹⁹	1.2 (1.2%)	69.1 (67.1%)	32.7 ^c (31.7%)	-	753.3	12.0%
TriDDMAN ²¹	7.1 (4.8%)	97.9 (66.0%)	43.4 ^c (29.2%)	-	3789	3.8%

^a DOP; ^b DBP; ^c NPOE; ^d NaTPB; ^e TOAB

Following solvent washes, each electrode was further cleaned using cyclic voltammetry on CH Instruments CHI660D Electrochemical Workstation. The cyclic voltammetry sequence was on the Pt electrode as the working electrode, Ag/AgCl double junction electrode (Orion #90-02-00) as the reference electrode (with 900003 outer filling solution), and stainless steel mesh counter electrode. The sequence was done in 0.5 M sulfuric acid with a 2 V pre-treatment for 2 minutes and 20 sweeps of 1.1 V to -0.23 V to 1.1 V at a scan rate of 0.1 V/s. After the cyclic voltammetry cleaning, the electrode was washed with DI water.

Finally, ISMs were deposited dropwise according to the drop amounts and volumes in Table 3. The deposition thicknesses were adjusted with further trials. After the last deposition, the ISMs were then allowed to dry overnight. The ISMs were originally pre-treated in 10⁷ ppb Ag⁺ overnight and stored in air when not in use. Later Ag⁺ ISM preparations involved using 10⁵ ppb Ag⁺ solution pretreatment overnight and stored in 400 ppb Ag⁺ solution when not in use. During NO₃⁻ ISM testing, the pretreatment concentration was lowered to 400 ppb Ag⁺-equivalents NO₃⁻ solution to lower the limit of detection and facilitate the detection of NO₃⁻ at 50-500 ppb Ag⁺ equiv. of NO₃⁻.¹⁶

Table 3. ISM Deposition Drop Amounts and Volumes

Ionophore Used	Deposition drop count	Deposition volume per drop (μL)
SI-2 ⁹	4	7
DTBBT ¹⁰	4	7
MBT ¹¹	4	7
Porphine ¹²	4	7
TetOAB ¹³	1	7
NI-6 ⁴	4	7
TetOAN ²²	4	7
TetDDAN ¹⁹	1	10
TriDDMAN ²¹	4	7

D. Open Circuit Potential Measurements

The open circuit potential (OCP) measurements were done on CH Instruments CHI660D Electrochemical Workstation with the ion-selective electrode as the working electrode and the Orion #90-02-00 as the reference electrode. Outer filling solution for the Orion #90-02-00 was either the provided Orion filling solution (#90003; potassium nitrate) for Ag⁺ testing or 0.033 M sodium sulfate for NO₃⁻ testing. OCP was measured in millivolts (mV). During measurement, the ion-selective electrode is exposed to each concentration of AgNO₃ solution and left until the signal settles on a potential reading (potential remains at ± 0.1 mV over 30 seconds). When doing the Ag⁺ detection testing, each ISM was OCP tested for reversibility by being exposed to DI water, 100 – 10⁶ ppb Ag⁺, and then the same sequence in reverse back down to DI water. This same test was then done at 50-500 ppb for multiple cycles until

further discussions and literature search shows that DI water accelerates the aging of ISMs.¹⁴ As a result, the OCP testing was done cycling through the Ag^+ and NO_3^- solutions without the DI water exposure.

III. Results and Discussion

A. Silver Ionophore Testing

ISMs of the 4 ionophores tested were made according to Table 2. Initial depositions were 4 drops of 7 μL each for all ISMs. The ISMs were tested for Ag^+ detection by exposing each ISMs over $100\text{--}10^6$ ppb Ag^+ for one ramp-drop cycle. As seen in Figure 2, SI-2 and DTBBT showed the best results with linear detection to $100\text{--}10^6$ ppb Ag^+ . MBT and Porphine show higher drift between the ramp and drop runs than SI-2 and DTBBT. The Porphine drop run shows a loss of linear detection of Ag^+ (R^2 of 0.7), which is due to the poor solubility of the ionophore resulting in the leaching of the ionophore. SI-2 showed sub-Nernstian response (38 mV/decade) with good reversibility as observed by the similar linear fits. DTBBT showed Nernstian response in the first ramp (57 mV/decade), but the drop run shows a lower slope of 51 mV/decade with a higher change in slope between ramp and drop compared to SI-2. This was thought to be due to the DTBBT ISM

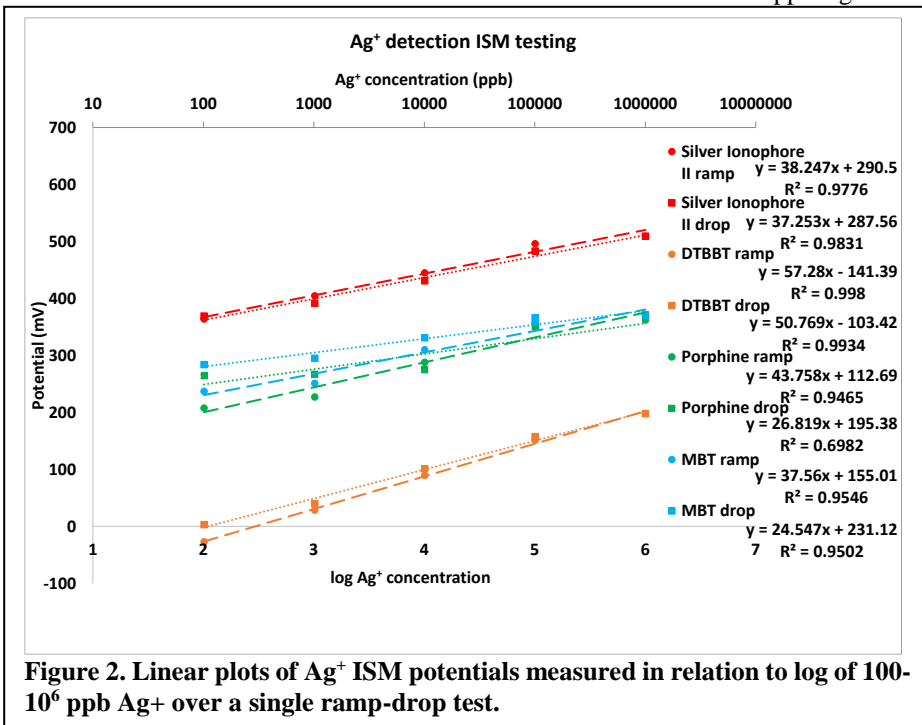


Figure 2. Linear plots of Ag^+ ISM potentials measured in relation to log of $100\text{--}10^6$ ppb Ag^+ over a single ramp-drop test.

being ran for the first time in the experiment and still required further cycles to stabilize the response behavior. The SI-2 was already ran for two ramp runs before this experiment. However, further testing of DTBBT showed downward drift with a second cycle having slopes of 56 mV/decade (ramp) and 39 mV/decade (drop) with lower R^2 values (0.95 and 0.87, respectively; data not shown).

Additional ISMs of SI-2 and DTBBT were produced to determine what conditions would improve the performance of the DTBBT ISM and SI-2 ISM. Initial trials were done focusing on finding deposition thickness and silver pretreatment concentration based on previous observations and literature. All Ag^+ ISMs have similar compositions in terms of the PVC (32-33%) and DOP (60-65%). The key difference between these ISMs is the ionophore and additives used, but as the PVC/DOP mixture makes up 93-96% m/m of the ISMs, optimization of the deposition thickness parameters were not considered separately for SI-2 and DTBBT. With 7 μL dropwise depositions, two groups of ISM thicknesses were made: original and modified. Original ISM thicknesses were made from four drops of either SI-2 or DTBBT solution, which were the ISM thicknesses used for Figure 2. The modified ISM thicknesses were made from either ten 7 μL drops of SI-2 or two 7 μL drops of DTBBT. It was originally thought that targeting 4 drops of DTBBT and 10 drops of SI-2 was preferred due to the initial success of DTBBT in Figure 2. However, Two SI-2 ISM depositions targeting the modified thickness failed to respond linearly to Ag^+ concentration and showed increased response times over 50-500 ppb Ag^+ (results not shown). As a result, 4 drops of SI-2 continued to be the original thickness due to the success the SI-2 original thickness ISM shown in Figure 2 over the modified thickness ISM. This was thought to be due to the thicker PVC membranes serving as an insulator, limiting the potential response of the ISM. For DTBBT ISMs, six DTBBT ISMs made with either the original (four ISMs) or the modified (two ISMs) thickness had failed to demonstrate a linear detection range of 50-500 ppb Ag^+ and, as a result, no further testing on DTBBT ISMs were done.

The other parameter of focus was pretreatment concentration. Pretreatments of the primary ion in the aqueous phase allow for the equilibration of the ISM with the aqueous phase and for the transport of primary ion in the membrane, resulting in a primary ion gradient within the membrane and replacing the positive ions of the ion exchange sites with the primary ion, Ag^+ .¹⁴ Literature reports pretreatment concentration ranges from 10^5 to 10^7 ppb Ag^+ , including literature reported by Casabo on SI-2 with a linear detection range down to 62 ppb Ag^+ with both 10^5 and 10^7 ppb pretreatment.⁹ With 20 hours of pretreatment, 10^5 ppb pretreatment and above is known to fully saturate the ISM while lower pretreatments can result in ion gradient in the ISM, depending on the thickness of the membrane.¹⁵ As a result, only 10^5 and 10^7 ppb pretreatments were considered to ensure Ag^+ fully saturates the ISM with overnight treatment. Too high of a pretreatment concentration could result in the release of Ag^+ in the ppb-level solutions that are used.¹⁵ As a result, the pretreatment was reduced to 10^5 ppb from 10^7 ppb. As a result, SI-2 deposition thickness was maintained at 4 drops of 7 μL and reduced pretreatment conditions from 10^7 ppb Ag^+ overnight to 10^5 ppb Ag^+ overnight.

Using these preparation conditions, SI-2 ISM was tested over 8 ramp-drop cycles to test for stable, linear detection of 50-500 ppb Ag^+ with exposure to DI water after each drop cycle as shown on Figure 3. The lower slope (29 mV/decade) of the ramp 1 indicates that ISM storage in 400 ppb Ag^+ increases the response time of the ISM as the potential of the 50 ppb Ag^+ solution is higher than the fitted line. This was due to the electrode being stored in 400 ppb Ag^+ and the membrane requiring additional time to equilibrate with the 50 ppb Ag^+ solution even with the less than ± 0.1 mV over 30 seconds rule. With each cycle, the fitted trendline shows slopes ranging from 39-43 mV/decade, a sub-Nernstian response. The intraday readings of the ISM were stable with 400 ppb measurements ranging from 336.1 to 339.5 mV. However, one week later, the same ISM was ran for an additional five cycles while continuing with DI water exposure after each drop cycle (Figure 3). These five cycles showed a significant drop in the potential measurements of the entire concentration range (Figure 4). For the 400 ppb measurements, SI-2 ISM showed a drop of 13 mV after 1 week of storage. Along with this potential drop, the ISM showed higher intraday variation with 400 ppb measurements ranging from 306.0 to 329.3 mV. This potential

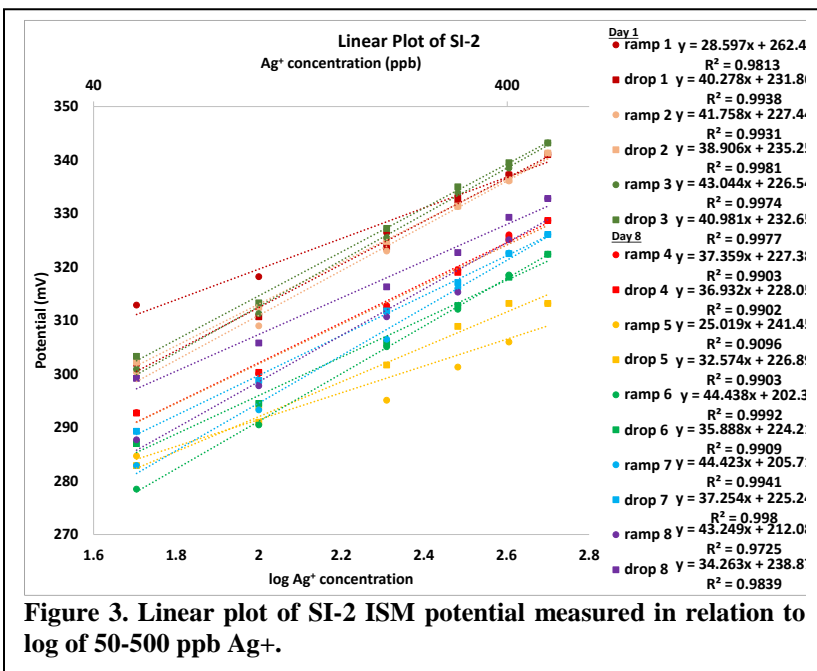


Figure 3. Linear plot of SI-2 ISM potential measured in relation to log of 50-500 ppb Ag^+ .

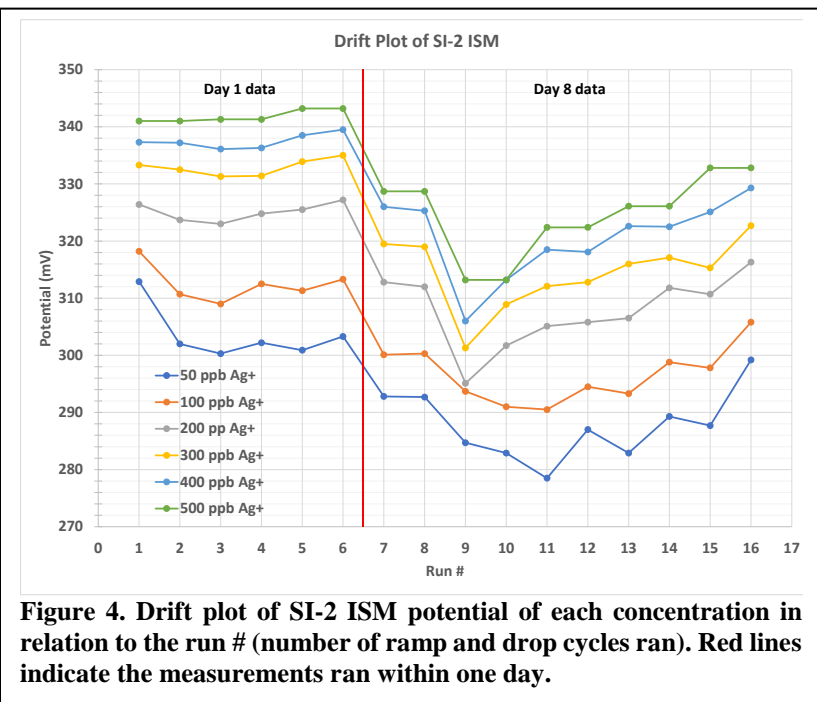


Figure 4. Drift plot of SI-2 ISM potential of each concentration in relation to the run # (number of ramp and drop cycles ran). Red lines indicate the measurements ran within one day.

drop and increased intraday variation behavior is summarized in the drift plot shown in Figure 4. The interweek potential drop indicates that the ISMs have yet to show stable potential responses as the first day's 200 ppb potential measurements are equal to the 400 ppb potential measurements done a week later. The intraday variation in potential is attributed to the repeated exposure of the ISM to DI water, resulting in the ISM's leaching of ionophore to the solution.¹⁴ Further testing of SI-2 ISMs will need to be done to confirm its usability as an ISM for the Ag^+ ChemFET, but as these ISMs have shown successful detection of Ag^+ over 50-500 ppb, focus was shifted to the nitrate ISM development and testing.

B. Nitrate Ionophore Testing and Selection

Five nitrate (NO_3^-) ionophores (TetOAB, TetOAN, Nitrate Ionophore VI, TetDDAN, and TriDDMAN) were purchased and tested for potential application as nitrate ISMs. The NO_3^- ISMs were made according to Table 1. Tests of the TetOAB and TriDDMAN ISMs did not show a Nernstian response to 50-500 ppb Ag^+ equiv. of NO_3^- as seen in Figure 5. For both ISMs, they were not considered for further studies due to their high limits of detection. TetOAB has a limit of detection higher than 500 ppb as the ISM does not show Nernstian response 50-500 ppb Ag^+ equiv. of NO_3^- with a slope of -4 mV/decade. TriDDMAN has a slope far below sub-Nernstian (-15 mV/decade). For TriDDMAN, it should be noted that the 200 ppb Ag^+ equiv. of NO_3^- measurement was considered an outlier due to contamination.

Nitrate Ionophore VI and TriDDMAN were also tested at the 10^2 - 10^5 ppb range as shown in Figure 6. TetOAN shows a Nernstian response above 400 ppb, but at below 400 ppb, a flat potential response. This result agrees with the expected 285 ppb limit of detection reported in the literature¹⁶. The behavior of Nitrate Ionophore VI is similar to TetOAN and agrees with the literature, which reports the limit of detection is estimated at 310 ppb with the lower linear range at 620 ppb.⁴ As a result, changes in the potential are minimal in the 100 to 400 ppb range (Figure 6). While running at higher concentration

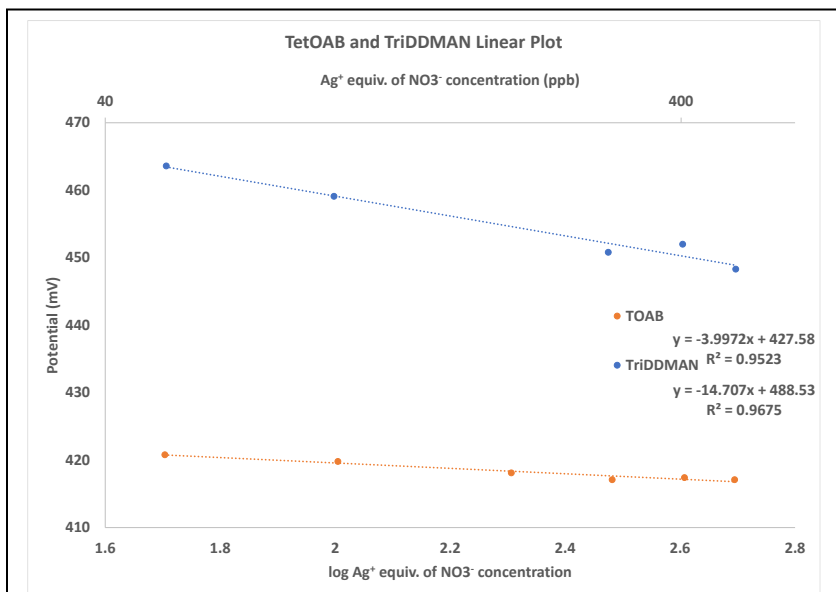


Figure 5. Linear plots of the TOAB (orange) and TriDDMAN (blue) ISM potentials measured in relation to log of 50-500 ppb Ag^+ equiv. of NO_3^- . The TriDDMAN 200 ppb measurement was removed as an outlier.

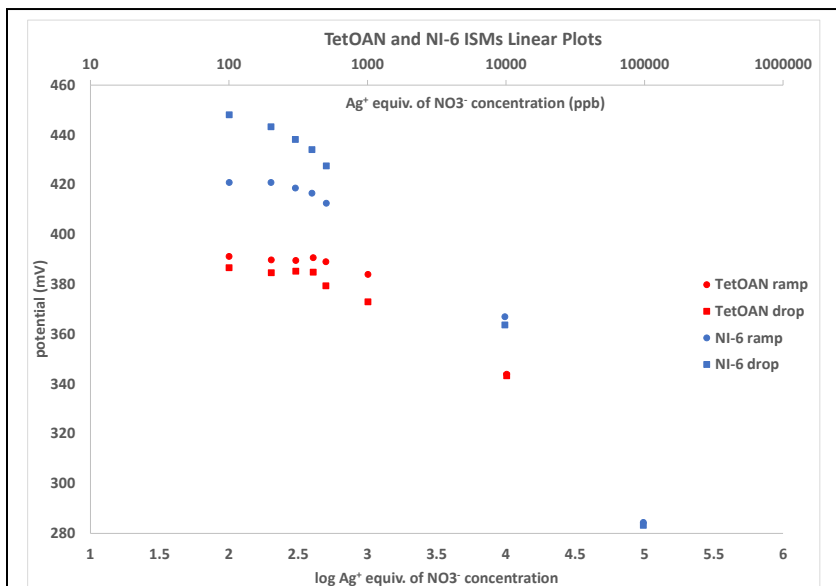


Figure 6. Linear plots of TetOAN (red) and Nitrate Ionophore VI (blue) ISM measured in relation to log of 10^2 - 10^5 ppb Ag^+ equiv. of NO_3^- .

ranges is within the linear range of these ISMs, it does not fit the needs of spacecraft potable water system applications (<400 ppb).

The last ISM to be discussed, TetDDAN, has reported success in the potable water system application range with a limit of detection of 108 ppb Ag^+ equiv. of NO_3^- .¹⁹ The results for TetDDAN ISMs are shown in Figure 7. TetDDAN ISMs have a linear range of 50-500 ppb Ag^+ equiv. of NO_3^- , fulfilling the requirements of the double ChemFET system. However, it should be noted that both ISMs display sub-Nernstian behavior with slopes settling around -15 to -20 mV/decade. This is a significant concern as small variations in the measured potential can greatly affect the concentration result. However,

adjustments in the ISM preparation can improve on this, such as increasing film thickness. Another issue observed in the TetDDAN is that the calibration curve continues to drift negatively with each day of measurements as shown in the drift plot in Figure 8. While intraday measurements stabilize with repeated cycles, interday measurements show a shift in potential due to drift as shown in the potential drops between the runs indicated by the red lines in Figure 8. One significant source of drift for ISMs found in literature is water penetration through the ISM and forming a thin water layer separating the ISM from the electrode surface and creating a reservoir of ions that lead to memory effects.^{23,24} Two methods for controlling the rate of water layer formation is through the increase of ISM layer thickness and the mixing of polytetrafluoroethylene (PTFE) particles into the ISM. ISM thickness increases the distance the water needs to travel through before forming the water layer on electrode, while hydrophobic PTFE particles block the paths that water can travel through the ISM. However, this source of drift cannot be prevented as water does need to flow through the ISM to allow the primary ion to diffuse into the ISM for detection. As a result, these solutions serves to extend the lifetime of the ISM, but drift remains a significant obstacle for long-term monitoring in aqueous solutions.

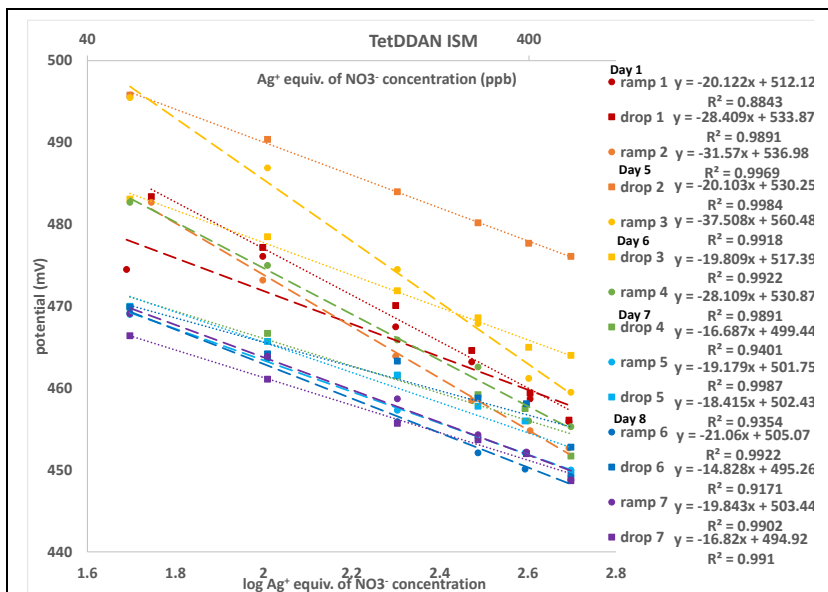


Figure 7. Linear plots of the TetDDAN ISM potential measured in relation to log of 50-500 ppb Ag^+ equiv. of NO_3^- .

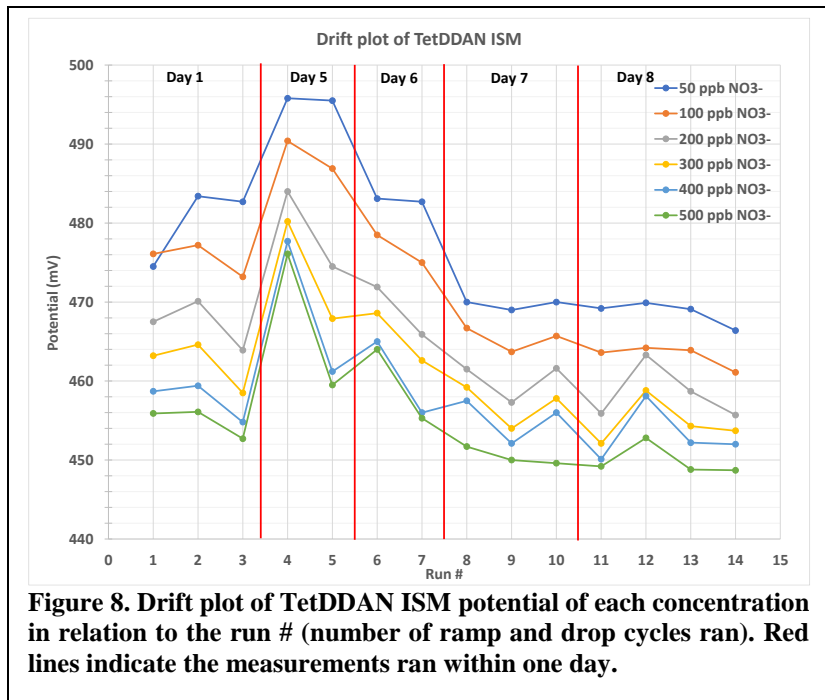


Figure 8. Drift plot of TetDDAN ISM potential of each concentration in relation to the run # (number of ramp and drop cycles ran). Red lines indicate the measurements ran within one day.

The doubling of the TetDDAN ISM thickness (Figure 9) resulted in a more Nernstian behavior with first 3.5 cycles performed on Days 1-3. It was originally thought that the increasing thickness of the ISM had increased the limit of detection to be higher than 50 ppb Ag^+ equiv. of NO_3^- , but it was later observed that there was a contamination in the 50 ppb solution. Remaking this solution shows linear detection down to 50 ppb Ag^+ equiv. of NO_3^- . However, the interday drift still remains and worsens after 8 days in storage as shown in Figures 9 and 10. On day 11 and afterward, the TetDDAN doubled thickness ISM showed greater intraday variation and overall downward trend in the potential measurements and slopes. This indicates that doubling the thickness fails to resolve the drift issue.

Early work with PTFE:PVC ISM is shown in Figure 11. However, these results show significant interday upward drift in potential, downward drift in slope, and an apparent loss of detection of the 50 ppb NO_3^- even with the solutions remade on Day 4. Some issues that contribute to the PTFE:PVC ISM drift and loss in 50 ppb sensitivity can primarily be attributed to poor distribution of the PTFE particles with potential of the particles aggregating during the drying of the ISM solution.

IV. Conclusion

The testing of 4 Ag^+ and 5 NO_3^- PVC-based ISMs made from formulations obtained from the literature is reported. The successful linear detection of 50-500 ppb Ag^+ was achieved using a SI-2 ISM, which is currently the leading Ag ISM for the Ag ChemFET. However,

repeated exposure to DI water impacted the stability of the Ag^+ measurements and the ISMs did show a significant potential drop after one week of storage, resulting in the 400 ppb potential range being equal to the 200 ppb measurements in the previous week. Further work will be required to improve on this drift.

The detection of 50-500 ppb Ag^+ equiv. of NO_3^- was accomplished using a TetDDAN ISM. However, TetDDAN shows high interday drift with the potential drifting negatively. This drift is a significant obstacle to the implementation of the dChemFET in spaceflight water monitoring as regular calibrations are required to correct for

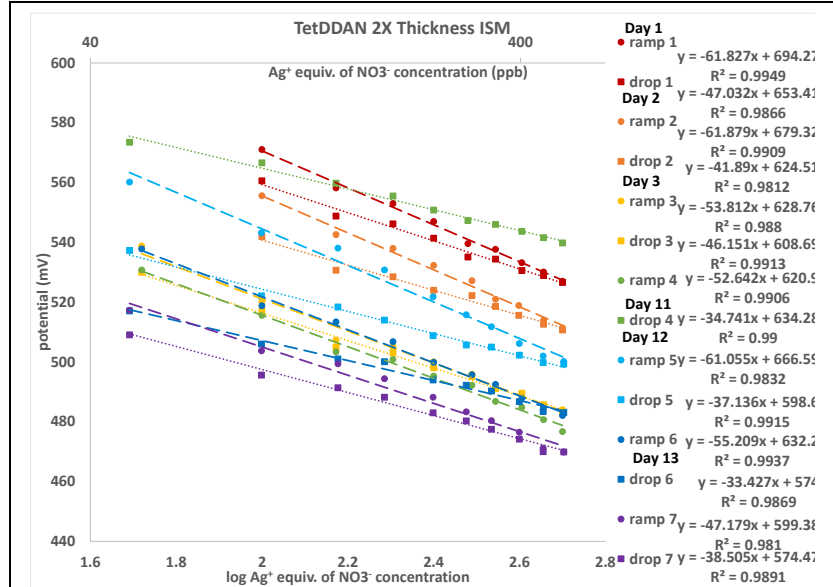


Figure 9. Linear plots of the TetDDAN Doubled Thickness ISM measured in relation to log of 50-500 ppb Ag^+ equiv. of NO_3^- . The 50 ppb measurements on ramp-drop cycles 1 and 2 were removed as outliers.

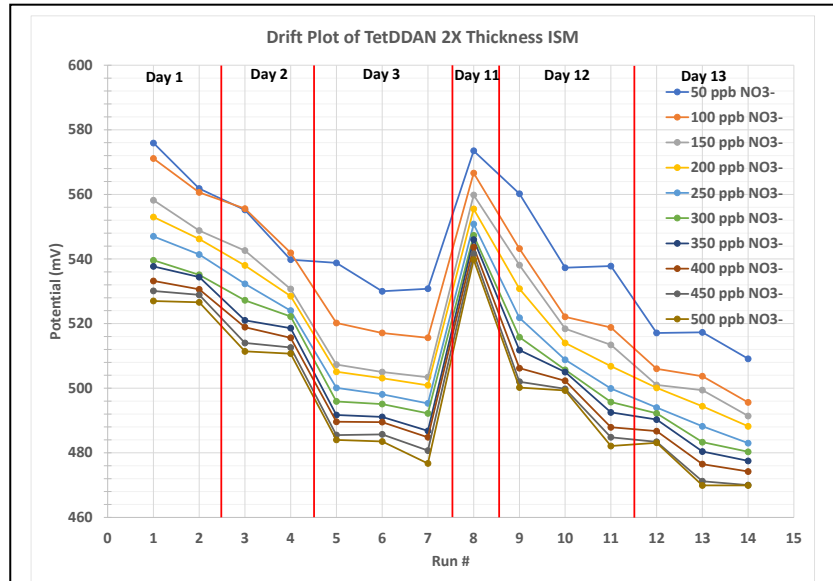


Figure 10. Drift plot of TetDDAN Doubled Thickness ISM showing measured potential of each concentration in relation to the run # (number of ramp and drop cycles ran). Red lines indicate the measurements ran within one day.

this drift. Doubling the TetDDAN ISM layer thickness fails to prevent this drift, but does improve the ISM by increasing the slope of the response to be closer to Nernstian behavior (-53 mV/decade). Recent work on reducing drift is being performed with mixing of polytetrafluoroethylene (PTFE) particles in the ISM to reduce water invasion forming a water layer between the ISM and Pt electrode, causing drift. However, these methods only serve to slow this process down and water layer formation cannot be fully prevented as water does need to flow through the ISM to allow the primary ion to diffuse into the ISM for detection. As a result, the dChemFET faces significant challenges due to interday drift and cannot be recommended for long-term silver biocide monitoring in the potable water system in spaceflight.

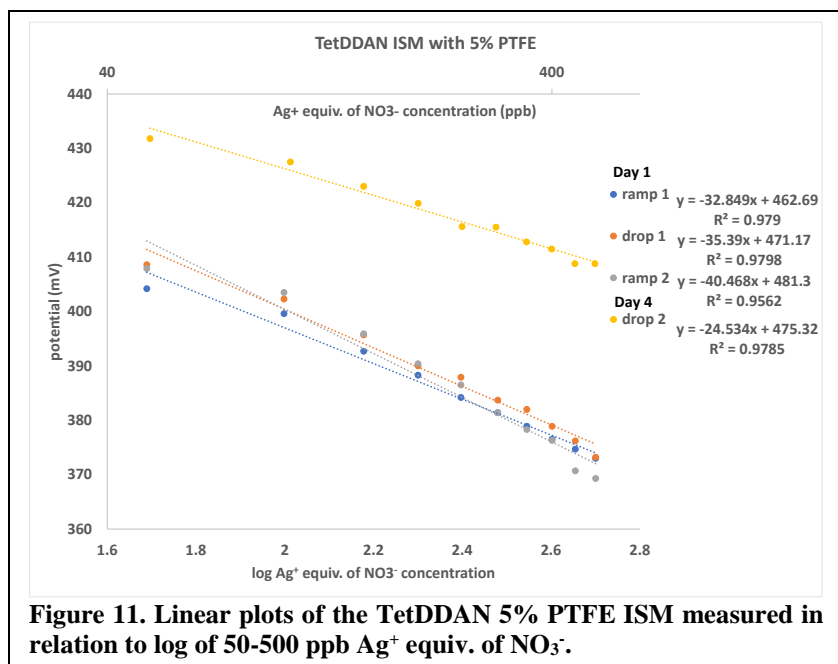


Figure 11. Linear plots of the TetDDAN 5% PTFE ISM measured in relation to log of 50-500 ppb Ag⁺ equiv. of NO₃⁻.

V. Future Work

The continuing issue of interday drift of the TetDDAN and SI-2 ISMs needs to be solved before the dChemFET project can be considered for continued development. Upon successful improvement of the ISMs in terms of interday drift, proof-of-concept testing of the dChemFET can be done in beaker and flow conditions to show successful detection of Ag⁺ against the NO₃⁻ ion as the reference measurement.

Acknowledgments,

The authors would like to acknowledge with special thanks to John Vance for his advice and help with the electrochemistry experiments and analysis.

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